Assessment of the Accuracy of the Quasiclassical Trajectories Approximation at a Low Collision Energy for the He−N_2 System

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We have computed rotational energy transfer differential and state-to-state integral quasiclassical cross sections for the He−N_2 system at 27.3 meV. By comparing these differential cross sections to close coupling ones, the accuracy of the quasiclassical approximation at such a low collision energy has been assessed as satisfactory.

Introduction

The He−N_2 Van der Waals system has attracted much attention lately, and more or less accurate potential energy surfaces have been developed [1−6]. Rotational energy transfer cross sections have been measured and computed both quantum mechanically and quasiclassically [1−3, 7−14]. Faubel et al. [9] have measured the rotationally elastic and inelastic differential cross sections (dcs) at the low collision energy of 27.3 meV. They have also performed close coupling (cc) calculations using the potential of Habitz et al. (HTT) [3]. These calculations have reproduced their experimental cross sections quite satisfactorily.

The above low energy results of Faubel et al. present a good opportunity to check the accuracy of the quasiclassical trajectories method at such a low energy vis-a-vis the cc calculations. The purpose of this paper is to present such a test as well as to give state-to-state integral cross sections for possible later use.

Technical Details

The employed method has been described previously for the He−N_2 system at 64 meV and with a single initial j [11]. The only difference in this case is that due to different experimental conditions, the initial energy distribution includes three rotational energy levels of N_2 rather than one. The populations of this distribution are: $j = 0$, 52%; $j = 1$, 33%; $j = 2$, 15%. That is, both the ortho and the para modifications are present in the calculation. Rather than using a weighted selection of initial j's, we have run three sets of trajectories, each set having a single initial j. The proportion of trajectories in each set is approximately equal to the experimental one. Thus we have run a total of 10333 trajectories, out of which 5373 have $j = 0$ ($\sim$ 52%), 3410 have $j = 1$ ($\sim$ 33%) and 1550 have $j = 2$ ($\sim$ 15%). In this way we are able to compute the total dcs as well as the elastic dcs's, the inelastic dcs's and the state-to-state integral cross sections for each initial j.

In the course of integrating each trajectory, among other things we keep track of the rotational energy (E_r). Within the region of strong interaction between the colliding partners, this energy usually oscillates going through one or more peaks before it settles to the final value it assumes outside this region ($E_{r\,fin}$). The largest of these peaks ($E_{r\,max}$) is saved in the output file for later use (see below).

Results and Discussion

For the computation of the cross sections we have used the HTT potential [3] which is the same one as used by Faubel et al. for their cc calculations [9]. This potential gives quite satisfactory scattering cross sections but it has been criticized as unable to reproduce accurately the bulk properties of He/N_2 mixtures [6, 15, 16]. In fact, most of the known He−N_2 potentials can reproduce accurately either

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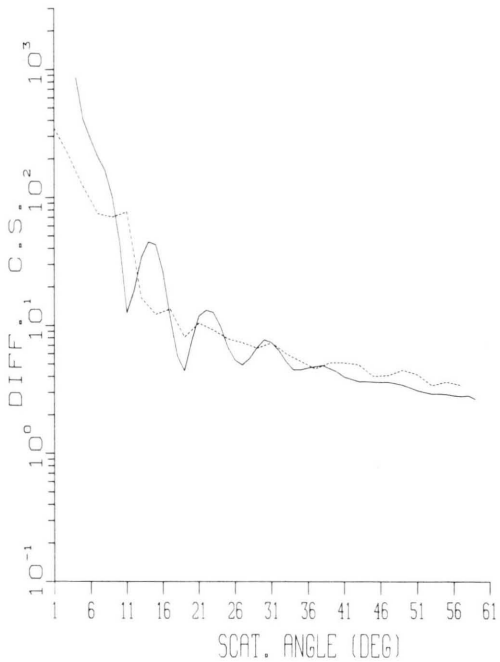

Fig. 1. Total dcs in Å²/sr; (——) cc, (– – –) quasiclassical; average error: 15.4% (the confidence limit is 90% for all figures).

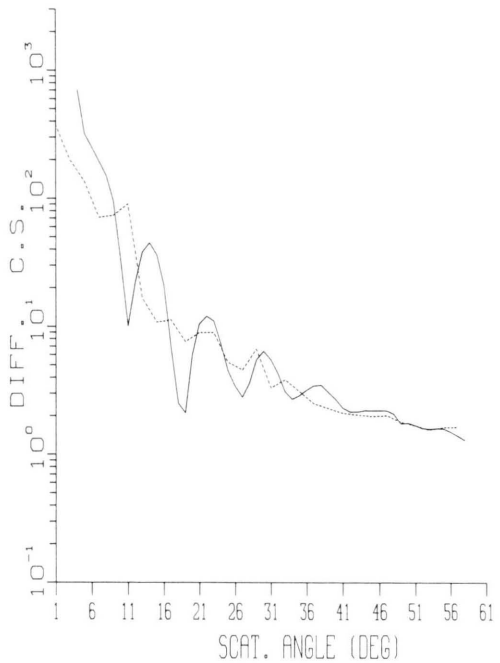

Fig. 3. 1 → 1 elastic dcs in Å²/sr; (—•—) cc, (– – –) quasiclassical; average error: 35.0%.

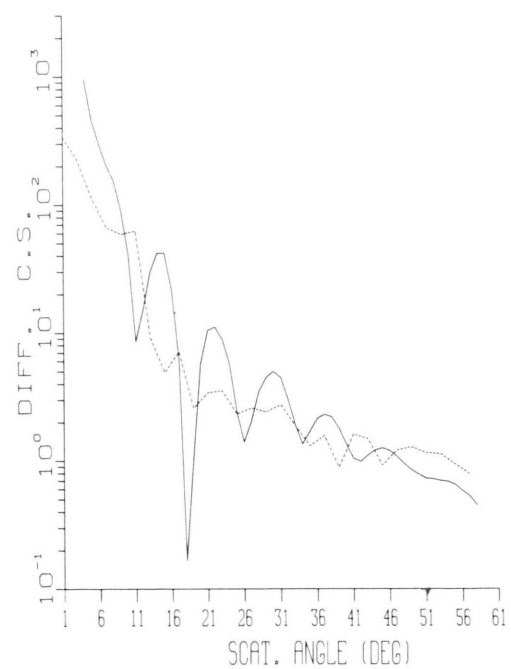

Fig. 2. 0 → 0 elastic dcs in Å²/sr; (——) cc, (– – –) quasiclassical; average error: 34.6%.

molecular beam scattering data or bulk property data but not both [16]. This has lead Gianturco and coworkers to develop a new potential [6] which reportedly gives results of comparable accuracy for both types of experiments. At any rate, since we are interested only in scattering data, the HTT potential is quite adequate although it is considered to be about 20% too shallow around the minimum [9].

Our results for the 0 → 0, 1 → 1, 2 → 2, 0 → 2, 1 → 3 and total dcs's are plotted along with the cc results of Faubel et al. in Figures 1–6. The latter data (from [9]) have been read for us out of the original plots in 1° intervals. We have made no attempt to smooth these data. The scattering angles shown in the figures are the centers of the employed angular bins (2° wide), and they represent center of mass scattering angles (χ_{cm}). The cross sections for small χ_{cm} (say $\chi_{cm} < 3$) appear in the above figures only for completeness. In Figs. 1–4, notice the classical rainbow structure around $\chi_{cm} = 12°$.

The state-to-state integral cross sections computed by both the direct and the proportional binning methods [11] are given in Table 1. The first method

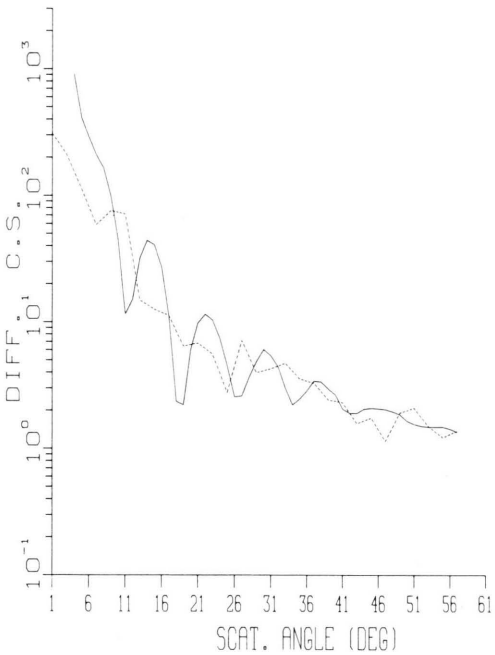

Fig. 4. 2 → 2 elastic dcs in Å²/sr; (——) cc, (– – –) quasiclassical; average error: 52.7%.

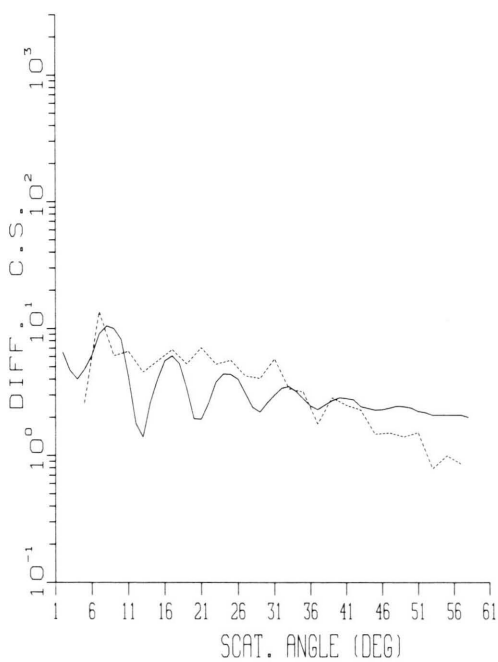

Fig. 5. 0 → 2 inelastic dcs in Å²/sr; (——) cc, (– – –) quasiclassical; average error: 37.9%.

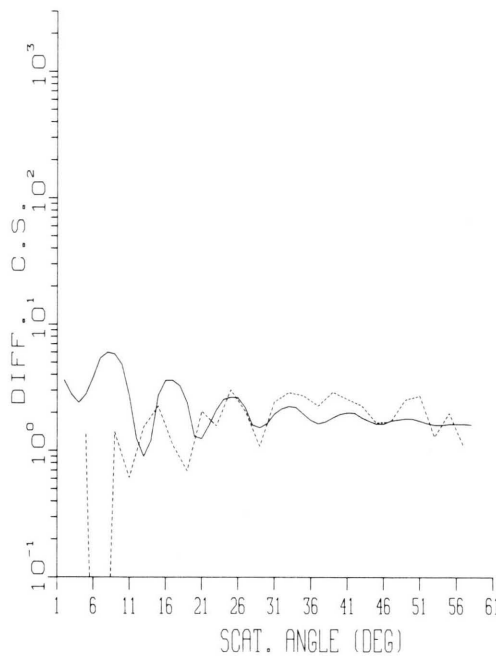

Fig. 6. 1 → 3 inelastic dcs in Å²/sr; (——) cc, (– – –) quasiclassical; average error: 65.9%.

corresponds to the usual scheme of assigning the final classical angular momentum j_c to one of two neighbouring bins, say j' or $j'+2$. In the second method, each j_c is "distributed" between j' and $j'+2$ in a proportional way depending on its position between them. Notice that for the $j=2$ case ($E_r \approx 1.52$ meV) the proportional binning method shows the correct excitation limit of $j'=10$ ($E_r \approx 27.89$ meV) while the direct binning method stops at $j'=8$.

Regarding the oscillatory behavior of E_r within the strong interaction region, it appears that for most trajectories the quantity $E = E_{r\,max} - E_{r\,fin}$ is a positive number. Thus, for $j=0$, 94.70% of the trajectories have $E>0$ while 0.26% have $E=0$; for $j=1$, 99.89% of the trajectories have $E>0$ while 0.09% have $E=0$; for $j=2$, all the trajectories have $E>0$.

We now turn to the comparison between the quasiclassical and the cc results. By examining Figs. 1–4 it becomes evident that the quasiclassical total and elastic dcs's agree satisfactorily with the corresponding cc dcs's. The 2 → 2 dcs appears

Table 1. State-to-state integral cross sections (in Å^2) computed by both the direct and the proportional binning methods. The % error corresponds to a 90% confidence limit.

j'	$\sigma_{0\to j'}$	% error	j'	$\sigma_{1\to j'}$	% error	j'	$\sigma_{2\to j'}$	% error
Direct binning method								
0	22.34	3.58	1	29.51	3.67	0	2.29	20.73
2	13.50	4.50	3	11.43	5.79	2	29.00	5.44
4	8.76	5.08	5	7.77	6.17	4	12.50	8.14
6	5.23	5.52	7	2.60	9.52	6	5.37	11.48
8	0.07	40.48	9	0.01	164.48	8	2.03	16.01
Proportional binning method								
0	24.70	2.92	1	29.77	3.19	0	11.29	9.12
2	13.13	3.06	3	13.39	3.30	2	22.16	5.35
4	8.04	3.80	5	6.01	4.96	4	11.54	5.67
6	3.55	4.93	7	1.94	7.62	6	4.72	8.70
8	0.49	8.85	9	0.20	16.35	8	1.42	13.67
						10	0.07	30.55

somewhat erratic mainly due to the small number of trajectories starting with $j=2$. The rotationally inelastic dcs's are compared in Figs. 5 and 6. Here, the degree of agreement is harder to assess due to the large errors ($\sim 38\%$ for the $0\to 2$ cross sections and $\sim 66\%$ for the $1\to 3$ cross sections). Nonetheless, the quasiclassical dcs's seem to be in the immediate vicinity of the cc ones. Thus one seems justified to say that at low collision energies where no less than 5 rotational levels may be excited, the quasiclassical trajectory approximation is still satisfactory.

This is a somewhat surprising conclusion because at least three necessary conditions for the validity of the quasiclassical approximation are not fullfilled in this system. These conditions are: a) The de Broglie wavelength must be small; b) the collision energy must be much larger than the excitation threshold; c) the internal (rotational) quantum numbers must be large. Such conditions have been discussed by Barg et al. [17], who have also established the validity of the quasiclassical approximation for the Li^+-H_2 system but at energies much higher than in the present case. The third condition above does not seem to be very important because it is not fullfilled in many cases including the present one and the one in [17].

A possible explanation of our results can be advanced by refering to the approximate analytic formulas for cross sections obtained by the Fraunhofer model for elastic and rotationally inelastic scattering [18]. This is a simplified IOSA type model which reproduces fairly well the position and magnitude of the peaks of the elastic and inelastic cross section oscillations. Thus, the relatively good agreement between the cc and the quasiclassical cross sections found here may be attributed to the anisotropy and softness of the potential, which dampen out the Fraunhofer oscillations [19].

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